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A Study of the Influence  
Of Heat upon the  
Common Household Fats

Chemistry

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**A STUDY OF THE INFLUENCE  
OF HEAT UPON THE  
COMMON HOUSEHOLD FATS**

BY

**TERESA RUTH BEROLZHEIMER**

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**THESIS**

FOR THE

**DEGREE OF BACHELOR OF SCIENCE**

IN

**CHEMISTRY**

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**COLLEGE OF SCIENCE**

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Teresa Ruth Berolzheimer

ENTITLED A Study of the Influence of Heat on the Common

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

Bachelor of Science

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## INTRODUCTION

The fact that fats are decomposed when heated has long been recognized by both housekeeper and chemist. The housekeeper noted that they become ill smelling and bad tasting and the chemist termed this change, rancidity. Brannt<sup>1</sup> says: "Rancidity is caused by the oxidation of the fats, which progresses at first slowly, then rapidly. The fats split into free fatty acids and glycerine, and by absorption of oxygen various volatile fatty acids (Propionic, butyric, etc.) are formed from the free acids and glycerin, imparting the characteristic taste and odor." Speaking of oleic acid, he says<sup>2</sup>: "Under ordinary atmospheric conditions it is decomposed on heating, yielding fatty acids, such as acetic, caprylic and a large quantity of sebacic. E. von Raumer<sup>3</sup>, under the subject of The Changing Content of Volatile Fatty Acids in Rancid Butter, shows the increase in Reichert - Meissel number and hence increase in content of volatile acids. H. Nördlinger<sup>4</sup>, discussing *Wie stark ranzig dürfen Speiseöle sein, bevor sie zu ~~genuss~~ zweicken unbrauchbar sind?*, says: "All vegetable oils, those contained in the seeds as well as those removed by pressing or extracting and those remaining in the cake after pressing, always contain a certain content of free fatty acid without becoming rancid." The average is 1.74%. Hence when the convention of the German Society for Industrial Chemistry placed the permissible maximum content of free fatty acids in table oils at 1%, almost all the European table oils were to be considered "rancid," even



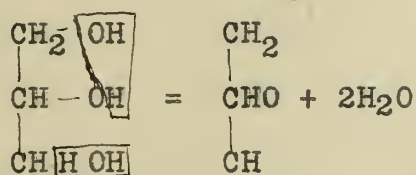
in the fresh condition. Williams<sup>5</sup> states that fats are not boilable but are decomposed when heated above 400°. R. Heinrich<sup>6</sup> defines rancidity as free acid to be determined by titration with n/20 KOH, results being calculated as oleic acid. A Scala<sup>7</sup> investigated lard, butter and olive oil, exposing them to the light and air. The iodine absorption number decreased, due chiefly to oleic acid. Glycerin also was liberated, and was then oxidized and transformed. E. Spaeth<sup>8</sup> in a Contribution to the Knowledge of the Rancidity of Fats, states as a result of work on lard, that rancidity on standing is due to light and atmospheric oxygen forming lower acids-free, with increase of volatile acids. Oxidized fats show lower iodine number and higher melting point. A. Scala<sup>9</sup> in Measurement of Rancidity of Fats other than Butter, states: "Finding that the determination of the free acid in oils and fats was not an absolute measure of rancidity, the author proposes the use of the Reichert-Wollny method for this purpose. Bornemann, Arata and the writer have previously called attention to the invariable presence of volatile acids in rancid fats. Lard, olive oil and stearin were exposed in flat basins, covered by large dishes, to the action of air and sun light; every fifteen days a determination of the total volatile acids by the Reichert-Wollny method, and free volatile acids by ~~the~~ distillation with water (5 grs. fat + 140 cc. H<sub>2</sub>O distill 110 cc.) were determined. All results are expressed as cc n/10 alkali per 5 grs. The writer proposes to call a fat rancid which contains volatile acids, and suggests that a limit of 2cc. be fixed, beyond which the fat should be considered no longer edible.





	Lard		Olive Oil		Stearin	
	Total Vol. Acids	Free Vol. Acids	Total Vol. Acids	Free Vol. Acids.	Total Vol. Acids	Free Vol. Acids
Fresh	0.0	0	0.0	0	0.0	0
15 days	0.6	0	0.2	0	0.8	0
30 "	0.8	0.2	1.0	0	0.9	0
45 "	2.5	1.5	1.5	0	1.8	0.4
60 "	4.0	1.6	2.8	0.4	2.0	0.6
75 "	5.2	2.3	3.2	0.8	2.3	0.8
90 "	7.8	4.6	3.3	1.1	2.5	1.8

Brannt<sup>10</sup> says: "Fats possess the characteristic property of decomposing when strongly heated and yielding thereby sharp acrid acrolein vapors of a disagreeable odor. Acrolein  $\text{CH}_2\text{CH}\cdot\text{CHO}$  is formed when fats are strongly heated or subjected to destructive distillation, chiefly in consequence of the decomposition of glycerin, water being separated.



Weigmann and Backe<sup>11</sup> also mention the decomposition of fat and the formation of free fatty acids in the ripening of cheese. The following method was found<sup>12</sup> for rancidity: 10 grs. fat are dissolved in 50cc. of a mixture (equal vols.) of ether and alcohol, and titrated with  $n/20$  NaOH, using phenol phthalin. 1cc. of alkali solution per 100 grs. fat used denotes 1° of rancidity. (Köttstörfer). Allen<sup>13</sup> says: "True fats and fixed oils are not



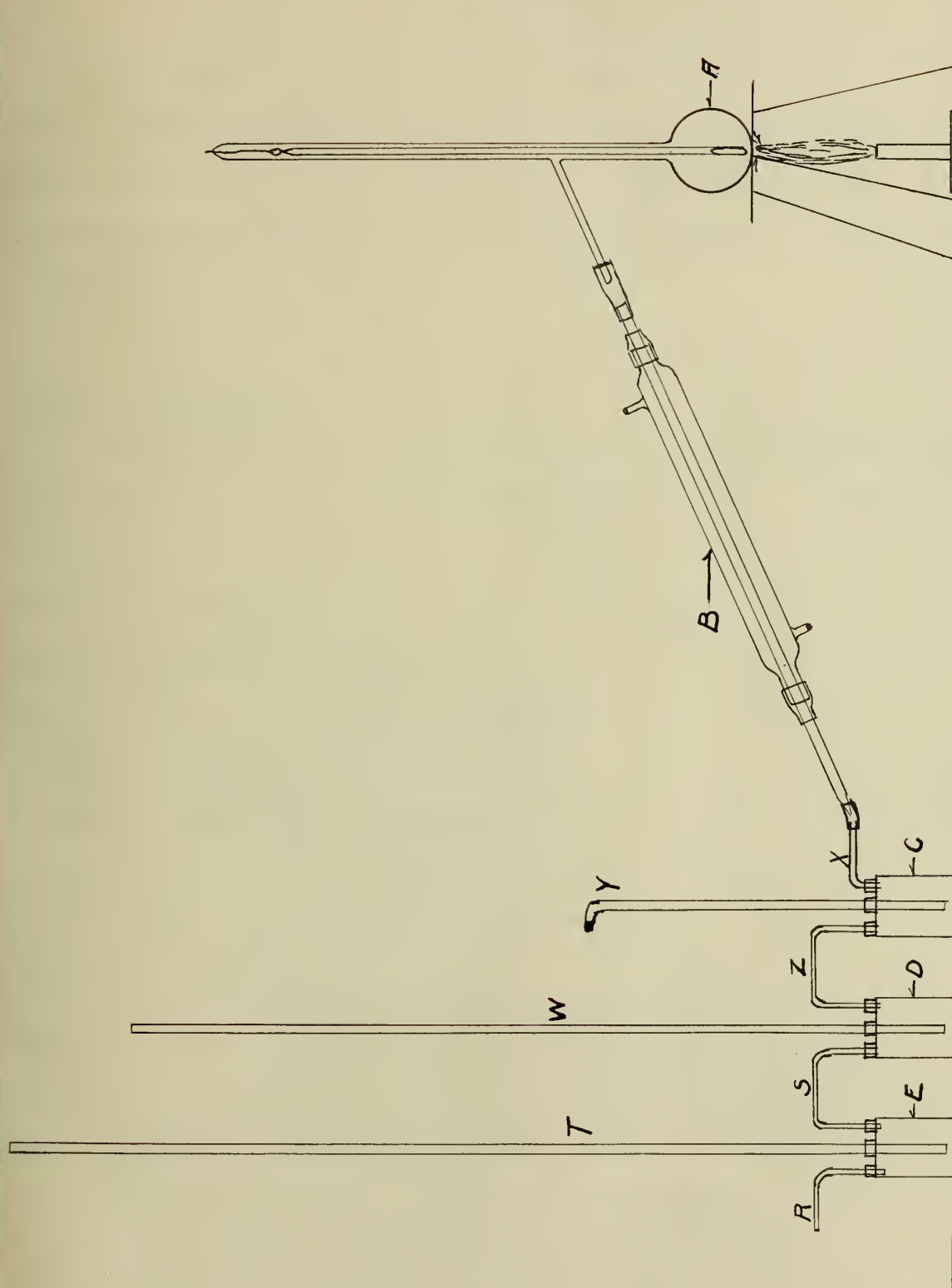
capable of being distilled without decomposition. When heated alone they darken and evolve acid, offensive odors; and when further heated to about  $315^{\circ}\text{C}$ . ( $600^{\circ}\text{F}$ .)  $\text{CO}_2$  is evolved, together with peculiarly irritating vapors of acrolein  $\text{CH}_2\text{CH COH}$ , various volatile organic acids, and gaseous, liquid, and solid hydrocarbons. The temperature at which these decompositions occur has been improperly called the "boiling point" of the oil, the phenomenon of apparent ebullition being really due to the escape of the gases formed by the decomposition. Rancidity<sup>14</sup> fats lose their color, acquire an acrid, disagreeable, taste and an acid reaction to litmus paper. V. Boulez<sup>15</sup> says: "The formation of rancidity in fats depends upon their hydrolysis, which is followed by the hydrolysis or saturation of the non-saturated fatty acids. The development of rancidity is hence really an autolysis of the unsaturated fatty acids and can take place only in the presence of moisture." Wiley<sup>16</sup> mentions the formation of acrolein at high temperatures and says that rancidity does not depend on the amount of free acid present. He cites the case of olive oil, which may contain as high as 3% free acid without becoming rancid.

#### OBJECT

The object of this investigation is to determine whether or not it is possible to gain some clue to the effect of heat on fats by means of the changes brought about in the chemical constants.







APPARATUS  
FIG. 1.



## EXPERIMENTAL

To accomplish the object mentioned, three fats, two samples of lard and one of beef suet, were heated to the "smoking" temperature, and the time, temperature, color and any other phenomena appearing were noted. Before and after heating, the fats were analyzed.

### Heating Experiments.

Considerable difficulty was encountered in getting a suitable vessel for use in the heating experiments. At first a copper retort, such as is used for generating oxygen, was employed. The joint between the can and neck was packed with asbestos, and the two screwed firmly together. Under the pressure generated, however, this leaked badly, and finally the whole neck was replaced by a two-holed rubber stopper, carrying a  $360^{\circ}\text{C}$ . thermometer and a bent glass tube leading to the condenser. The rest of the apparatus is as shown in Figure 1. B is a Liebig condenser, C, D and E are three-holed Wolff bottles. C is an empty receiver connected with the end of the condenser by means of the bent glass tube which reaches to the bottom of the bottle. The tube Y reaching to the bottom and being plugged at the upper end was intended to convey a blast of air, if necessary to force out the volatile acids. D and C are connected by the tube Z passing just thru the cork into C and to the bottom of D. This bottle contains 50 cc. of a solution of  $\text{KH SO}_3$ , 12 grs. per liter. This is to remove the acrolein formed in the heating, and might also serve as a means of quantitative determination if necessary.





The safety tube <sup>W</sup> takes care of back pressure, and the tube S connects with the flask E. This flask contains 30 cc. of a standard solution of NaOH to absorb volatile acids. It is provided with safety and outlet tubes.

With this apparatus experiment No. 1 was carried out. The heat was applied very slowly, and, when the fat had completely melted, the flame was raised to about four inches and kept there except when otherwise noted.

Sample No. 2		EXPERIMENT 1
Time	Temperature	Remarks
9:30	Start	Copper container closed with two-holed rubber stopper carrying thermometer and delivering tube of glass.
9:53	208°	Fumes visible in bend of the glass tube
	220°	Distillation quite distinct.
	224°	
9:59	265°	Real distillation
	270°	
10:03	293°	
10:12	295°	Distillate is clear and slightly yellow
10:13	300°	
10:21	307°	
10:26	307°	
10:40	360°+	Sudden rise.

Sample No. 2 is a one pound sample of lard A bought in the open market. It was kept in a refrigerator when not in use, to insure its freshness.

The experiment lasted 1 hour and 10 minutes, with a change



in temperature of over  $360^{\circ}$ . Twenty-three minutes were required for the first  $208^{\circ}$ , with a steady rise. Six minutes were required for a rise of  $57^{\circ}$  from  $208^{\circ}$ - $265^{\circ}$ , while  $23^{\circ}$  were passed in 4 min.  $293^{\circ}$  was held for 10 minutes. Then there was a rapid rise of  $5^{\circ}$  to  $300^{\circ}$ , and from there gradually to  $307^{\circ}$ . After staying at  $300^{\circ}$  for five minutes, the thermometer thread shot up suddenly above  $360^{\circ}$ .

The whole distillation seemed quite - no disturbance being heard inside the retort, and this sudden rise was unaccompanied by any startling change except an apparent cessation of fumes, seeming to indicate completion of the reaction. The flame was immediately turned out. When cooled some liquid was found remaining in the retort. No change in color could be noted because of the character of the container. The rubber was badly melted and scorched, but did not leak since it stuck tight to the side of the vessel. To prevent this scorching, an attempt was made to pack the cork in asbestos paper. One unsatisfactory experiment, however, served to show that this did not prevent scorching, and, moreover, allowed leaking. Dr. C. W. Balke then suggested that a distilling bulb with a thermometer fused in the neck be used. Two flasks were prepared, as shown in Fig. 1,A, one carrying a  $360^{\circ}$  and the other a  $550^{\circ}$  thermometer. A  $550^{\circ}$   $\text{CO}_2$  pressure thermometer was used in order to register the sudden rise from  $307^{\circ}$  to  $360^{\circ}$  and beyond.





Sample 2 (reheated)

## EXPERIMENT 2

Time	Temp.	Color	Remarks
4:06	Start		
4:45	241°	Yellow	Heating quietly.
	250°	Brown	Bubbles in the flasks.
4:50	263°		Fumes not abundant but increasing.
4:57	275°		Slowly bubbling.
5:02	292°		Bubbles every 5 sec., fumes begin to condense.
5:04	304°	Dark Brown	Bubbles come in groups. Liquid dark brown on upper surface.
5:10	360°+		Sudden rise.

This container was entirely satisfactory. The thermometer registered the temperature of the fat during the experiment, while the glass allowed complete observation at all times. This experiment lasted one hour and four minutes, consuming 39 min. in a rise of 241°. Here again there was a pause at 263°-275°, at which decomposition seemed most marked. The rate of rise from 292°-304° seemed more rapid than in Experiment 1 and the length of stay at 304° was shorter. Again a rapid rise from 304°-360°+ was noted. This time the contents of the flask could be closely watched. There seemed to be no change whatsoever. There was no evolution of gas, no explosion, no change in color, the liquid remaining transparent golden brown.



## Sample 2 (reheated)

## EXPERIMENT 3

Time	Temp.	Color	Remarks
9:30			
	60°	Golden brown	Fat Completely melted.
9:50	184°	"	
9:55	202°	"	Fumes visible in flask; flow of bubbles in absorption flasks irregular; some absorbed in the flasks.
10:05	220°	"	
10:10	235°	"	Liquid condensing in upper part of flask and in side neck. Fumes come from surface of liquid, not in bubbles from the bottom.
10:20	255°	"	
10:27	280°	"	
10:32	290°	"	Rather copious fumes.
11:33	295°	"	Flame raised to prevent back pressure.
11:45	303°	"	
12:00	303°	"	Flame turned out.

This experiment lasted two hours and fifteen minutes, the rate of change being much slower than in the two preceding ones. 360° was not reached. Decomposition began at a lower temperature and continued more evenly than before. Throughout the whole time the action was quiet, there being no violent evolutions of gas.



## Sample 2 (reheated)

## EXPERIMENT 4

Time	Temp.	Color	Remarks
2:35			
2:45	185°		
2:55	241°		Heating quietly
3:22	286°		Bubbles coming regularly in absorption flasks
3:30	290°		
3:32	300°		

Again 290° is registered as a stopping place. The rate of rise is much the same as in Exp.1. 365° was not reached.

## Sample 2 (reheated)

## EXPERIMENT 5

Time	Temp.	Color	Remarks
8:50	52°	Brown	Crackling heard in flask, probably distillation of acrolein.
	140°	"	More crackling.
9:12	230°	"	Fumes seen.
9:21	280°	"	Copious fumes.
9:30	337°	"	Very sudden rise.
9:32	360°+	"	Shot up suddenly.

Experiment 5 had a more rapid rate of rise than any of the others. Instead of one, two very sudden changes are noted, one from 280°-337°, the other from 337°-360°. The action was quiet after the slight crackling disappeared.





## Sample 2

## EXPERIMENT 6

Time	Temp.	Color	Remarks
3:06		White	
3:37	210°	Yellow	Slight darkening. Flame slightly raised.
3:50	240°		Fumes visible
4:04	250°		
4:10	260°		Copious fumes.
4:20	304°		
4:45	320°		
4:48	360°+		Sudden increase.

This experiment was performed to answer an objection that was raised as to the rapid rise in temperature from 304° or thereabouts to 360° and above. A fresh portion of the one-pound sample of lard A was used, and heated in the same way as before. The time of heating was one hour and 41 min., of which 31 min. were necessary to raise it to 210°. Two rapid changes of temperature are noted, one from 260°-304°, the other from 320°-36°, this last one being a sudden jump. This corresponds quite closely to the results of Exp. 5, when the same sample had been heated four successive times. This similarity between them and the fact that both differ from the experiment with fresh, new fat, is probably partly explained by the fact that this second fresh sample had been kept for several months, although in the cold and dark, and some change had taken place. The temperature change in cooling was also noted this time. At 4:53 the thermometer dropped suddenly to 304° and then lowered gradually to 240° at 4:55.

This rapid rise in temperature seemed to need explanation,



and, since none was at hand, it was determined to find out if possible what it meant and to see if any other fats would give the same result. To determine also what the exact temperature was, the 550° CO<sub>2</sub> pressure thermometer was sealed into its flask.

Sample 4		EXPERIMENT 7	
Time	Temp.	Color	Remarks
8:30			2 in. wide flame.
8:45			Flame sharpened.
9:26		Light yellow	Flame raised slightly
9:33	181°		Bubbles come off with rapid and loud detonation.
9:50	197°	Straw colored	
9:59	204°		Rapid, loud detonations; fat darkens perceptibly on the upper outside edges. More large bubbles given off rapidly and with a loud noise.
	221°		Light brown flakes sink to the bottom from surface. Intermittant sputtering.
10:40	240°		Still sputtering.
10:50	242°		Flame turned out. Sputtering continued.

Sample 4 is a 5-pound sample of lard B. In color, consistency and general appearance, it could not be distinguished from lard A. It is reported to be a "pure lard rendered in tanks under pressure, and is the standard grade sold on the Chicago Board of Trade."

The results of the heating experiments on the two samples are markedly different, - the most striking perhaps is the evo-





lution of gas. In all the previous experiments the heating proceeded quietly, with only one case of crackling, and that at the temperature of  $52^{\circ}$ . All decomposition came from the surface of the liquid and gas formed passed off from there. Moreover, the formation of flakes was slow and the flakes small. In this experiment (No.7), the gas was formed at the bottom of the flask and in large bubbles which passed off with explosive force and sound. The first explosion was noted at  $181^{\circ}$ , considerably above the temperature at which water vapor is supposed to pass off, yet it might possibly have been the last traces. However, at  $204^{\circ}$ ,  $221^{\circ}$  and  $240^{\circ}$ , where the explosions and sputterings were most marked, it seems hardly possible that even a trace of moisture could have been present. The explosions, moreover, were accompanied by a marked increase in the number of dark brown flakes appearing. This indicated plainly that decomposition was taking place, and producing a substance, volatile at the temperature of the explosion. N-valeric acid boils at  $186^{\circ}$ , when pure, but when mixed with other fatty acids it might well have its boiling point lowered and boil at  $181^{\circ}$ . Similarly, n-caproic acid boils at  $205^{\circ}$  and may have come off at  $204^{\circ}$ . Ceananthylic acid boils at  $223^{\circ}$ , hence may have caused the explosions at  $221^{\circ}$ , while caprylic acid with a b.p. of  $237^{\circ}$  may possibly have come off at  $240^{\circ}$ .

The difficulty and slowness with which this fat heated was also marked. After 2 hours and 20 minutes, the temperature was only  $242^{\circ}$ , a point reached in considerably less than an hour in all experiments with l a r d A . . . Of this time, one hour was required to reach  $181^{\circ}$ , accomplished in previous cases in less than 30 minutes. There seemed to be no clearly marked point



of decomposition, although much took place at 221°, a much lower temperature than that previously noted.

## Sample 5

## EXPERIMENT 8

Time	Temp.	Color	Remarks
8:45	melted	Light yellow	Brown flakes floating in the liquid. Slight crackling heard intermittently.
10:20	194°	Brown	Heating quietly. Flame raised slightly.
10:26	211°	"	
10:28	212°	"	Explosive distillation. Loud noise.
10:36	229°	"	
10:40	234°	"	Intermittent, heavy explosions.
10:50	236°	"	

Sample No. 5 is the product of Exp. 7, lard B after it had been heated to 242° once. This time the heating proceeded even more slowly than before, 1 hour and 35 minutes being consumed in raising the temperature to 194°, while in the previous case it was 1 hour and 20 min. Thirty minutes more of increased heat raised it only 40°, making a total of 236° in 2 hours and 5 min. This final result is approximately the same as in Exp. 7, where 242° were reached in 2 hours and 20 minutes. Explosive evolution of gas was again noted, this time even more marked than heretofore. The bubbles were very large and each time an increased number of brown flakes resulted.



## Sample 6

## EXPERIMENT 9

Time	Temp.	Color	Remarks.
2:45	50°	Cream	Mass semisolid. Some crackling.
3:00	76°	Straw	Slight "
3:07	92°	"	" "
3:12	112°	"	
3:14	114°	"	
3:19	115°	"	Bubbles rise from suspended matter.
3:27	116°	"	" given off with a crackling sound.
3:29	120°	"	" " " " " "
3:30	126°	"	" " " " " "
3:31	132°	"	Small bubbles given off from suspended matter.
3:32	136°	"	Bubbles given off explosively.
3:35	148°	"	
3:36	156°	"	Bubbles, crackling.
3:40	160°	"	
3:43	165°	"	
3:49	166°	"	
3:50	168°	"	

This experiment was performed to get some idea of the rapidity of rise at the lower temperatures. Sample No. 6 is the product of Exp. 8, lard B heated to 242° and 236°. The experiment lasted 1 hour and 5 minutes, the temperature rising 168° in that time. The crackling at 50° probably is due to acrolein, L & P. There is a pause at 114° and 115° of 5 minutes and 8 minutes respectively, accompanied by the evolution of some gas. At 120° the temperature rose to 126° in 1 minute, gas being evolved at the





same time. Successive rapid rises follow, the temperature increasing 126°-132° in 1 minute, from 132°-136° in 1 minute and 148°-156° in 1 minute, each change being accompanied by an evolution of gas.

Sample No. 7

# EXPERIMENT 10

Time	Temp.	Color	Remarks
9:15			
9:42	180°	Straw	Quiet
9:54	180°	Light brown	Quiet.
9:59	184°	"	Flame raised slightly.
10:02	187°	"	
10:05	189°	"	Heating quietly.
10:18	190°	"	
10:22	200°		
10:33	227°	"	
10:40	229°	Darkening	Quiet
10:45	230°	"	
10:51	234°	"	"

Because of the very marked difference in the action of lards B and A during heating, it was decided to try a fresh sample of the latter. Sample No. 7 is a 3-pound <sup>un-</sup>opened bucket of lard A. The experiment lasted 1 hour and 36 minutes, and was characterized throughout by quiet decomposition, all of which seemed to come from the surface. In point of temperatures noted, this experiment compares very well with Experiment 3 on the earlier 1-pound sample.



EXP. 3. (Sample 2)		EXP. 10 (Sample 7)	
Time	Temp.	Time	Temp.
9:30		9:15	
		9:42	180°
9:50	184°	9:59	184°
		10:02	187°
		10:05	189°
		10:18	190°
9:55	202°	10:22	200°
10:05	220°	10:33	227°
		10:40	229°
		10:45	230°
10:10	235°	10:51	234°

The rate is different, however, sample 7 heating a great deal slower, 1 hour and 36 minutes to 40 minutes for sample 2 (reheated). In 1 hour the temperature in Experiment 3 had risen to 290°.

In all of these last experiments the heating has been slow and the rise in temperature not very great. In no case has 300° or more been reached. Experiment 11 was performed in order to see if the temperature could be forced to rise above 300°





Sample No. 8

## EXPERIMENT 11

Time	Temp.	Color	Remarks
2:10		Golden brown	Start
3:39	232°		Heating quietly
2:46	239°		" " Some surface distillation.
2:50	240°		
2:59	242°		
3:01	243°		
3:15			Flame slightly raised.
3:23	250°		
3:26	258°		Fumes seen in flask.
3:31	265°		
3:34	268°		
3:40	269°		Fumes seen in flask.
3:50	271°		Fumes seen in flask. Slight bubbling and sputtering. More crackling.
3:55	272°	Darker	
4:07	279°		
4:36	282°		
5:02	290°		Quiet
5:10	293°		
5:24	295°		
5:34	300°		
5:36	304°		

Sample 8 is the product of Experiment 10 and shows in this experiment the same characteristic quietness. At 271°-279° there is a very slight crackling, sputtering and subsequent darkening



of the liquid, indicating rapid decomposition. Capric acid boils at 270° and might easily come off with slight explosive force at 271-2°. A comparison with previous experiments on this brand of lard shows marked resemblances.

Exp. 11		Exp. 1		Exp. 2		Exp. 3		Exp. 6	
Time	Temp.	Time	Temp.	Time	Temp.	Time	Temp.	Time	Temp.
2:10		9:30		4:06		9:30		3:06	
2:39	232°					10:10	235°		
2:46	239°								
2:50	240°							3:50	240°
2:59	242°			4:45	241°				
3:01	243°								
3:23	250°				250°			4:04	250°
3:26	258°					10:20	255°	4:10	260°
3:31	265°	9:59	265°	4:50	263°				
3:34	268°								
3:40	269°		270°						
3:50	271°								
3:55	272°			4:57	275°				
4:07	279°								
4:36	282°					10:27	280°		
5:02	290°					10:52	290°		
5:10	293°	10:02	293°						
5:24	295°	10:12	295°			11:33	295°		
5:34	300°	10:13	300°						
<u>5:36</u>	<u>304°</u>	<u>10:21</u>	<u>307°</u>	<u>5:04</u>	<u>304°</u>	<u>11:45</u>	<u>303°</u>	<u>4:20</u>	<u>304°</u>
3hrs.26min.51min.				58 min.		2hrs.15min.		1hr.14min.	



This table shows a striking number of temperature repetitions; 240° occurs twice, 250° three times, 265° twice, 290° twice, 293° twice, 295° three times, 300° twice, and 304° three times. There are also a number of results that are so close as to be practically coincident. In all cases the most marked decomposition was between 260° and 300°, with a narrower limit of 260°-280°. The rate of rise is markedly different, varying from 3 hours and 26 minutes in Exp. 11 to 51 minutes in Exp. 1. One noticeable fact in Experiment 11 is that there was no rise from 304° to 360°+ as in all previous experiments on this brand. In fact all efforts to reach this point in the manner noted before were absolutely without avail. Only once more was this temperature even reached, and then it was approached gradually. What the sudden shoot upwards may mean cannot be stated nor can an explanation be given for its appearance or non-appearance.

In order to intensify any chemical reactions occurring during the heating, No. 8 was reheated in

Sample 8 (reheated)			EXPERIMENT 12
Time	Temp.	Color	Remarks.
8:55		Brown	
9:40	200°		Smoking.
10:05	280°		Temperature remained stationary for some time.
10:55	300°		
10:57	303°		
11:01	304°		

The noteworthy points in this table are the temperatures





280°-300° and 304°, and also the length of time held at 304°, i.e. 4 minutes, and the rate of rise, which was 2 hours, 6 minutes, comparable with Exp.3.

In all the heating experiments with lard B, the temperature had not risen above 242°, so an effort was made to force the temperature up and see what would happen. Sample No. 6 used in Exp. 9, the product of Exp. 5 and already heated to 242° and 236° at two different times, was again used.

Sample 6 (reheated)

# EXPERIMENT 13

Time	Temp.	Color	Remarks
3:45			
4:10	110°		Considerable crackling.
4:30	275°		Smoking quietly.
5:10	317°	"	"
5:45	333°	"	"

This heating resulted in a temperature of 333°, reached gradually and without much disturbance. 275° seems to be common to both lards but 304° is not recorded at all for lard B and 360° does not seem to be attainable.



Sample No. 7

## EXPERIMENT 14

Time	Temp.	Color	Remarks
8:43	Start		
10:00	193°	Light brown	Heating quietly
10:26	196°		" " . Some surface distillation.
12:00	194°		" "
8:50			
9:40	197°	Brown	Heating quietly
9:44	204° 205°		" " Some surface distillation.
9:59	221°		
10:12	229°		Crackling and slight explosion.
10:32	239°		" " " "
10:34	240°		" " " "
10:40	244°		
11:00	245°		
1:00			
3:06	247°		
3:20	251°		
3:45	253°		
4:10	261°		
4:30	265°		
5:20	267°		
5:55	267°		

This experiment was performed to prepare a third long period





sample for analysis. It is continued in Exp. 15, sample 9 being the result of Exp. 14.

Sample No. 9			EXPERIMENT 15
Time	Temp.	Color	Remarks
9:25			
10:11	245°		Heating quietly
10:25	257°		" "
10:55	259°		" "
1:15			
1:45	244°		
5:43	277°		

The extremely slow rate of rise is the remarkable item in these two experiments.

Sample 11			EXPERIMENT 16
Time	Temp.	Color	Remarks
2:20			
2:40	240°	Light yellow	Heating quietly
2:43	250°		
2:55	268°	Darkening	Fuming.
4:20	270°		Raised flame slightly.
4:56	320°		Dark flakes appear.
5:15	340°		
5:20	350°		
5:35	360°+		" " "

Sample 11 is one of beef suet, home rendered, kidney fat being



rendered at the lowest possible temperature. The product was yellow-white, very firm and hard when cold .

This experiment is noteworthy for the long pause at  $268^{\circ}$ - $270^{\circ}$ . Of the whole time, 3 hours, 15 minutes, 20 minutes were necessary to reach  $240^{\circ}$ , 35 minutes to  $268^{\circ}$ , the temperature remaining constant at this point for one hour, twenty-five minutes, during which time decomposition was constantly going on. When a little more heat was applied, the temperature rose gradually to  $320^{\circ}$  in 36 minutes, then to  $340^{\circ}$  in 19 minutes, and above  $360^{\circ}$  in 15 minutes more. This is the first time  $360^{\circ}$  has been reached subsequent to the experiments on sample No. 2, and this is a gradual increase not a sudden one.

#### Analytical Work.

To determine the changes in chemical constants that had taken place during heating, analyses were made of the fresh fat and of the products of some of the experiments. Only those determinations were made as gave promise of showing a distinct variation. These were,

- I Specific Gravity.
- II Iodine Absorption Number.
- III Total Free Acids.
- IV Free Volatile Acids.
- V Soluble and Insoluble Acids.
- VI Reichert-Meissel Value.



## Methods of Analysis

Wherever possible the methods were those of the Association of Official and Agricultural Chemists:

I Specific Gravity<sup>17</sup>. A specific gravity flask of 25-30cc. capacity without attached thermometer, is thoroughly washed with water, alcohol and ether, and dried. After cooling, weigh accurately bottle and stopper. Fill the flask with freshly boiled, hot distilled water, insert stopper carefully and place in a bath of hot distilled water so that the joint is covered. Keep the bath boiling briskly for a few minutes, then remove ~~xxxxx~~ the flask, cool and weigh when the temperature of the balance is reached. Empty, rinse with alcohol and ether, and dry for a few minutes at the temperature of boiling water. Fill the flask with dry, hot fat, being careful to exclude air bubbles. Insert stopper and place in a boiling water bath. After a few minutes remove, cool to the temperature of the balance and weigh.

$$\text{The specific gravity} = \frac{\text{weight of fat}}{\text{weight of water}}$$

## II. Iodine Absorption Number.<sup>18</sup>

### A. Reagents.

#### 1. Hübl's iodine solution.

Dissolve 26 grs. c.p. I in 500 cc. 95% alcohol. Dissolve 30grs.  $\text{HgCl}_2$  in 500 cc. 95% alcohol. Filter the latter if necessary, and mix the two solutions. Let mixed solutions stand 12 hours before using.

#### 2. Sodium Thiosulfate solution.

Dissolve 24.8 grs. c.p.  $\text{Na}_2\text{S}_2\text{O}_3$  freshly pulverized as





finely as possible, and dried between filter paper, and dilute with  $H_2O$  to 1 litre at temperature at which titrations are to be made.

### 3. Starch solution.

Boil 1 gr. starch in 200 cc.  $H_2O$  for 10 min. and cool to room temperature.

### 4. Potassium iodide solution.

Dissolve 150 grs. of K I in  $H_2O$  and make up to 1 litre.

### 5. Decinomal potassium dichromate solution.

Dissolve 4.9083 grs. c.p.  $K_2Cr_2O_7$  in  $H_2O$  and make up to 1 litre at temperature of titrations. The bichromate should be checked against pure Fe.

## B. Procedure.

### 1. Standardizing $Na_2S_2O_3$ sol.

Place 20 cc. of the  $K_2Cr_2O_7$  solution to which has been added 10 cc. of the K I solution in a glass stoppered flask. Add 5 cc. strong HCl, allow the solution of  $Na_2S_2O_3$  to flow slowly into the flask until yellow color of the liquid has almost disappeared. Add a few drops of starch paste and with constant shaking continue to add  $Na_2S_2O_3$  solution until color just disappears.

## C. Determination.

Not more than one gram of fat is weighed into the bottle and 10 grs. chloroform added. After complete solution has taken place, add 30 cc. of iodine solution in the case of fats and 40-50 cc. in the case of oils. Place the bottles in a dark place and allow to stand, with occasional shaking, for three hours. This time must be closely adhered to in order to get good results.



The excess of iodine should at least be as much as is absorbed. 20 cc. of KI solution and 100 cc.  $H_2O$  are added to the contents of the flask. Any iodine on the stopper should be washed back into the flask with KI solution. The excess of I is now titrated with  $Na_2S_2O_3$  solution, which is run in gradually, shaking until the yellow color of the solution has almost disappeared. A few drops of starch paste are added and the titration continued until the blue color has entirely disappeared. Close the flask and shake violently to allow KI to absorb any I held in chloroform. A sufficient amount of  $Na_2S_2O_3$  should be used to prevent the re-appearance of blue color for five minutes. At time of adding I to fat 2 flasks of same size should be employed for conducting the operation without fat. Blanks should be carried out just as experiments are; and must be made each time I solution is used. Keep temperature constant.

$$\text{Percent I absorbed} = \frac{\text{Na}_2\text{S}_2\text{O}_3 \text{ to I absorbed} \times \text{Na}_2\text{S}_2\text{O}_3 \text{ in I}}{\text{weight of fat}} \times 100$$

### III. Total Free Acids.<sup>19</sup>

#### Solutions.

1. Neutral alcohol.
2. n/10 NaOH.

#### Procedure.

10 grs. of the sample are weighed into a flask, add 50 cc. 95% alcohol which has been neutralized with weak NaOH, using phenolphthalein as indicator, heat to boiling point. Shake to dissolve all free fatty acids. Titrate with n/10 alkali, shaking until faint color remains.





1 cc.  $n/10$  NaOH = 0.0282 grs. oleic acid. Expressed often as acid number, number of milligrams required to neutralize 1 gram of fat.

#### IV. Free Volatile Acids.<sup>20</sup>

##### Solutions.

1. Boiled distilled  $H_2O$ .
2.  $n/10$  NaOH. Pumice.

##### Determination.

Weigh 10 grs. sample into a flask and treat with 130 cc. warm distilled water. Connect with a Liebig condenser, and distil into 110 cc. flasks in 40 minutes. Rinse into Ehrlenmeyer flasks and titrate with  $n/10$  NaOH. Express as number of mg. NaOH required for 5 gr. fat.

#### V. Soluble and Insoluble Acids.<sup>21</sup>

##### Solutions.

1. Standard NaOH.
2. Alcoholic Potash. Dissolve 40 grs. c.p. KOH in 1 litre 95% alcohol, which has been distilled from KOH. The solution must be clear and the KOH free from carbonates.
3. Standard acid.

##### Procedure.

Place about 5 grs. of the sample in a 250 cc. Ehrlenmeyer flask, add from a pipette 50 cc. of alcoholic potash solution and saponify by heating on the water bath, after closing the flask with a stopper carrying a reflux condenser. Run 2 blanks at the same time. After complete saponification remove the condensers



and evaporate the alcohol by further heating. Titrate the blanks with standard HCl, using phenolphthalein as indicator. Run into each of the flasks containing the saponified fat one cc. more of  $n/2$  acid than is necessary to neutralize the alkali in the blanks. Connect with a reflux condenser, and heat on the steam bath until the separated fatty acids have collected in a layer. Cool the flask in ice water until the fatty acids have solidified; then decant the liquid through a dry filter, taking care not to break the cake. Add about 200 cc.  $H_2O$  to the flask, insert the cork with condenser and heat again on the water bath until cake of acids is thoroughly melted. During the process the flasks should be occasionally agitated with a circulatory motion in such a way that its contents are not allowed to touch the cork. When the fatty acids have again separated/into an oily layer, cool and filter into the litre flask. Repeat three times. Make up to the mark and titrate 100 cc. portions with standard NaOH. Calculate amount of acid in total, deducting the excess used.

Insoluble acids (Hehner value) . Allow the flasks containing the cake to drain on the filter paper for 12 hours, then transfer the cake with what can be removed from the paper to a weighed glass evaporating dish. Rinse out the flask and wash the filter paper with hot, strong alcohol, allowing all washings to run into the dish. Evaporate the alcohol by placing on the water bath. Dry the dish in the water oven for 2 hours, cool and weigh. Repeat and reweigh until constant.





VI. Reichert-Meissel Value.<sup>22</sup>

## Solutions.

1. Neutral 95% alcohol.
2. NaOH solution (1:1). Dissolve 500 grs. NaOH in 500 cc.  $H_2O$ .
3. Pumice.
4.  $H_2SO_4$ . Mix 200 cc. con.  $H_2SO_4$  with 1000 cc.  $H_2O$ .
5.  $n/10$  NaOH.

## Determination.

Weigh out samples of 5 grs. each into 250 cc. Erlenmeyer flasks. Add 10 cc. neutral alcohol and 2 cc. NaOH solution (1:1). Attach a reflux condenser, and heat on the water bath with occasional shaking until saponification is complete. This is shown by the clearness of the solution and its freedom from fat globules. Evaporate the alcohol by removing the condenser and heating the flask on the bath. The last traces of alcohol may be removed by waving the flask briskly, mouth down, - to and fro.

Dissolve the soap by adding 135 cc. of recently boiled distilled water to the flask and warming on the water bath with occasional shaking until solution is complete. When the soap solution has cooled to about  $60^\circ$ , set the fatty acids free by adding 5 cc. dil.  $H_2SO_4$  (2:10). Connect the flask with the reflux condenser and heat in the water bath without boiling until the fatty acid emulsion forms an oily layer on the surface of the liquid. Cool the flask to room temperature, and add a few pieces of pumice to prevent bumping. Connect the flask with a glass condenser and distil at such a rate that 110 cc. of the distillate will be collected in 30 minutes. Collect the distillate in 110 cc. graduated flasks in the neck of which is a short stemmed funnel





provided with a loose plug of absorbent cotton to serve as a filter. Pour the distillate into flasks add phenolphthalein and titrate with  $n/10$  NaOH. The number of cc. of  $n/10$  NaOH solution required to titrate the soluble fatty acids distilled from 5 grs. fat under the conditions of the experiment is known as the Reichert-Meissel number.

"To obtain concordant results in the determination of the Reichert-Meissel value, all the details of the process must be standardized; variations in any of the conditions lead to variations in the results. Especially the duration of saponification greatly influences the results; the longer the period, the higher the Reichert-Meissel value obtained. This appears to be due to the polymerization of the acids. Saponification by glycerol yields to lower value than saponification by alcohol, probably because at the higher temperature some of the acids are completely decomposed. The figure for insoluble acids on the other hand, is always higher with glycerol than with alcohol, and in saponifying with glycerol in using the Polensky process for cocoanut oil there is always a liability to error." <sup>23</sup>

In accordance with these suggestions, alcohol was used as the saponifying agent, and the time was uniform for all determinations at 7 hours. 110 cc. was distilled in 40 minutes instead of 30 minutes. Standard NaOH contained .00710 grs. NaOH per cc.

.050055 grs. Oleic Acid. Standard HCl contained .03935 grs HCl.



## Results of Analyses

### Specific Gravity Determinations

Sample Number	Weight of Fat	Weight of H <sub>2</sub> O	Specific Gravity.	Temperature.
4	23.8383	26.6668	.8939	100°C
6	23.9494	"	.8981	"
8	23.9802	"	.8993	"
7	23.8609	"	.8946	"
9	23.8316	"	.8937	"
11	23.7726	"	.8915	"
10	23.8768	"	.8954	"
12	23.8535	"	.8945	"

The table shows the results of all the sp. gr. determinations. Results on separate samples of heated and unheated fats are as follows:

Sample No. 4 is lard B unheated, and Sample No. 6 is the same after having been heated a total of 7 hours, 30 minutes to 242°, 236°, 168° and 333° at four different times.

	No. 4	No. 6	Diff.
Sp. Gr.	.8939	.8981	+.0042

This sample shows a rise of .0042.

Sample No. 7 is the three-pound sample of lard A.

Sample No. 8 is the same after it had been heated a total of 7 hours, 8 minutes, once to 234° and twice to 304°.

Sample No. 9 was a fresh one heated a total of 10 hours,



23 minutes, and to 194°, 245° and 261° at the different times.

Sample No. 10 reached a total of 16 hours, 21 minutes in five heating experiments of 194°, 245°, 267°, 259° and 277°, respectively.

Sample Number	Hours Heated	Specific Gravity.	Difference from Unheated
7	0	.8946	
8	7	.8993	+.0047
9	10 1/3	.8937	-.0009
10	16 1/3	.8954	+.0008

No. 9 shows a drop in sp. gr., while No. 10 is an increase again. This seems to indicate that the increase in sp. gr. is not dependent on the length of time of heating.

Sample No. 11 is unheated beef suet, while No. 12 was heated 3 hours, 15 minutes, to 360°+.

Sample Number	Hours Heated	Specific Gravity	Difference from Unheated
11	0	.8915	
12	3 1/4	.8945	+.0030

Here again there occurs a marked increase.





## Total Free Acid Determinations

Sample Number	Fat taken, Grams.	NaOH used, cc.	Acid Value, mgs.per gr.	Acid as Oleic %	Acid Value, Average	Oleic Value, Average
1A	9.4800	12.56	9.40	6.63		
1B	13.5384	18.24	9.56	6.74	9.48	6.68
2A	12.3188	1.65	.943	.67		
2B	10.4326	1.32	.898	.63	.920	.65
4A	8.8481	.55	.441	.32		
4B	11.0655	.70	.448	.32	.444	.32
6A	8.6090	4.84	3.99	2.84		
6B	10.2394	5.68	3.94	2.87	3.965	2.855
8A	8.6507	6.55	5.37	3.83		
8B	11.3105	8.26	5.19	3.69	5.28	3.76
7A	9.1217	.57	.443	.32		
7B	11.1410	.70	.446	.32	.444	.32
9A	10.9082	2.20	1.43	1.01		
9B	10.9931	2.24	1.45	1.02	1.44	1.015
11A	9.2511	.90	.691	.49		
11B	12.0338	1.20	.708	.50	.700	.495
10A	9.2671	3.45	2.64	1.88		
10B	10.7819	4.03	2.65	1.88	2.645	1.88
12A	13.7920	9.45	4.86	3.46		
12B	10.7316	7.50	4.96	3.53	4.91	3.495

Sample No. 1 is lard A, heated for a total of 6 hrs. 8 min.

360° was reached three times, 300° once, and 303° once.

Sample No. 2 is the unheated lard.



Sample Number	Hrs. Heated	Acid Value	Diff.	Oleic Acid	Diff.
1	6	9.48		6.68	
2	0	.920	+8.56	.65	+6.03

A marked increase in free acid is noted after 6 hours heating.

Sample Number	Hrs. Heated	Acid Value	Diff.	Oleic Acid	Diff.
4	0	.444		.32	
6	7 1/2	3.965	+3.521	2.855	+2.535

A comparison of the percentage increase in free oleic acid contents shows 10.77% for lard A and 12.62% for lard B.

Sample Number	Hrs. Heated	Acid Value	Diff.	Oleic Acid %	Diff.	% Diff.
7	0	.444		.32		
8	7	5.28	+4836	3.76	+3.44	9.30
9	10 1/3	1.44	+1.00	1.015	+.695	4.60
10	16 1/3	2.645	+2.201	1.88	+1.56	

Here, as in the sp. gr. determination, there is a large increase in No. 8, a much smaller one in No. 9 and a slightly larger increase in No. 10. No. 9 did not drop to a minus quantity.

Sample Number	Hrs. Heating	Acid Value	Diff.	Oleic Acid %	Diff.
11	0	.700		.495	
12	3 1/4	4.91	4.21	3.495	3.000

Beef suet also shows a great difference.  
Nos. 4 and 7 are identical here.



## Iodine Absorption Number Determination

Samp. No.	Weight of Fat Taken	I Sol. Used	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Used by Blank	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Used by Fat	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <del>to</del> to I Absorbed	I Abson No., grs. per 100grs. fat	Aver- age.	1cc. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <del>I</del> .01035 grs I
4A	1.0585	40	51.79	2.5	49.29	48.40		
4B	1.1463	"	"	.28	51.51	48.51	48.46	
6A	.6526	"	48.44	15.34	33.20	52.17		
6B	.0325	"	"	32.05	16.39	52.20	52.19	
8A	.5053	"	45.38	19.87	25.51	52.25		
8B	.7026	"	"	10.45	34.93	51.45	51.85	
7A	.6908	"	44.05	6.60	37.45	56.11		
7B	.7046	"	"	6.30	37.75	55.45	55.78	
9A	.5469	"	41.13	19.20	21.93	41.50		
9B	1.0183	"	"	.34	40.79	41.56	41.53	
11A	.8664	"	40.22	12.98	27.24	32.54		
11B	1.2228	"	"	1.75	38.47	32.57	32.56	
10A	.7900	"	39.85	12.07	27.78	36.40		
10B	1.0954	"	"	1.30	38.55	36.42	36.41	
12B	.6615	"	39.35	19.11	20.04	31.36		
12A	1.1918	"	"	4.20	35.15	30.52	30.94	

The relation between the different samples of the same fat is as follows:





Sample No.	Hours Heated	Iodine No.	Difference
4	0	48.46	
6	7 1/2	52.19	+ 3.73
7	0	55.78	
8	7	51.85	- 3.93
9	10 1/3	41.53	-14.25
10	16 1/3	36.41	-19.37
11	0	32.56	
12	3 1/4	30.94	- 1.62

Several peculiar phenomena are brought out in this table. The heating of lard B for 7 1/2 hours serves to increase the iodine number 3.73. On the other hand a similar heating of lard A decreased the iodine number a corresponding amount, and further heating augments the decrease. An addition of 3 hours, increasing from 7 to 10 hours heating, gives an added decrease of 10.32, while twice as many additional hours, 10 to 16, serve to augment the decrease in <sup>the</sup> iodine number only 1/2, i.e. 5.12.

Beef suet also shows a decrease in iodine number quite in proportion to that of lard A if the decrease is at all proportional to the length of time of heating.

7 : 3.93 = 3 1/4 : 1.82, while the decrease found is 1.62.



## Free Volatile Acid Determination.

Sample No.	Fat Taken grs.	NaOH cc.	Acid No. Mg. NaOH per 5 grs. Fat	Average
4A	10.4346	.13	.442	
4B	8.8238	.11	.442	.442
6A	8.4514	.08	.369	
6B	10.6139	.11	.368	.369
8A	8.8683	.15	.600	
8B	9.6985	.17	.601	.601
7A	9.1004	.10	.390	
7B	10.6200	.12	.401	.396
9A	13.0818	.13	.352	
9B	9.7645	.11	.399	.376
11A	13.2571	.16	.428	
11B	8.4966	.11	.450	.439
10A	10.7025	.13	.431	
10B	11.2785	.14	.441	.436
12A	10.8184	.11	.361	
12B	11.4824	.12	.369	.365



The relations between the different samples of the same fat are shown in the following table:

Sample Number	Hours Heated	Free Vol. Acids	Difference
4	0	.442	
6	7 1/2	.369	-.073
7	0	.396	
8	7	.601	+.205
9	10 1/3	.376	-.020
10	16 1/3	.436	+.040
11	0	.439	
12	3 1/4	.365	-.074

In this determination lard B shows a decrease, beef suet a decrease, and lard A shows, with the exception of sample No. 9, a marked increase. No. 9 shows a decided decrease.

In view of the high heat and length of heating, it was thought that some volatile acids passed into the outlet flasks during heating. Accordingly 30 cc. NaOH were introduced into the second flask and titrated after the experiment. Since the amount of fat in the flask was not known, the percentage cannot be given. It will be expressed merely as grs. NaOH used in the whole time.

No. 9 - .029082 grs. NaOH.

10 - .00325 " "

11 - .002617 " "

Even though this is not expressed as ~~the~~ the acid value it serves to indicate the relatively large amount of free volatile acid that passed off during Experiment 14.





## Soluble Acid Determinations.

Samp. No.	Fat taken grs.	HCl Used by Blanks	HCl Used by Fat Soap, cc.	NaOH Used by 100 cc.	Tot. NaOH Used by 1 l. - excess HCl. grs.	Sol. Acids. %	Average.
4A	5.2566	32.5	33	.40	.005845	.265	
4B	5.1477	32.5	"	.38	.004569	.212	.239
6A	6.0606	32.75	33.25	.50	.012225	.462	
6B	4.5051	"	"	.43	.008359	.436	.459
8A	6.2295	32.60	33.60	.70	.005310	.118	
8B	3.6027	"	"	.645	.00181	.12	.119
7A	3.8274	32.56	33.06	.43	.007759	.484	
7B	5.2671	"	"	.49	.011238	.50	.492
9A	6.2656	32.64	33.14	.50	.012225	.466	
9B	6.4499	"	"	.51	.012612	.467	.467
11A	4.3228	32.75	33.25	.40	.005793	.320	
11B	6.7296	"	"	.45	.009035	.321	.321
10A	5.1450	33.35	33.85	.89	.037107	1.722	
10B	4.8659	"	"	.86	.035193	1.727	1.724
12A	4.5681	32.85	33.35	.40	.005845	.306	
12B	4.5114	"	"	.40	.005857	.310	.308

1cc.HCl = .03935grs.HCl. 1cc.NaOH=.00638 grs.HCl.  $\frac{C_3H_7COOH}{HCl} = 2.3878$

This table shows the soluble acid determinations as taken.

The following table shows the relations between the several samples of the various fats:



Samp. No.	Hours Heated	Soluble Acids	Difference
4	0	.239	+ .220
6	7 1/2	.459	
7	0	.492	
8	7	.119	- .373
9	10 1/3	.467	- .025
10	16 1/3	1.724	+1.232
11	0	.321	
12	3 1/4	.308	- .013

The first sample of lard shows a marked increase, while the second sample, with one exception, shows a decrease. The increase of 1.232 in Sample 10 seems unaccountably large, while the decrease of .373 in Sample 8 also seems rather large. Beef suet shows a decrease of .013, corresponding with No. 9.



## Insoluble Acid Determinations

Sample No.	Fat Taken grs.	Wt. of Acids grs.	Insol. Fatty Acids, %	Average
4A	5.2566	4.8915	93.05	
4B	5.1477	4.7999	93.23	93.14
9A	6.2295	5.9518	95.54	
8B	3.6027	3.4407	95.50	95.52
6A	6.0606	4.8152	79.45	
6B	4.5051	3.5866	79.60	79.53
7A	3.8274	3.6426	95.25	
7B	5.2671	5.0163	95.23	95.24
9A	6.2656	6.0156	96.17	
9B	6.4499	6.2171	96.39	96.28
11A	4.3228	4.0894	94.60	
11B	6.7296	6.3261	94.71	94.66
10A	5.1450	4.9258	95.74	
10B	4.8659	4.6581	95.73	95.74
12A	4.5681	4.3958	96.23	
12B	4.5114	4.3422	96.25	96.24





The following table gives the results of different samples of the same fat:

Sample No.	Hours Heated	Insol. Acids	Difference
4	0	93.14	
6	7 1/2	79.53	-13.61
7	0	95.24	
8	7	95.52	+ .28
9	10 1/3	96.28	+ 1.04
10	16 1/3	95.74	+ .50
11	0	94.66	
12	3 1/4	96.24	+ 1.58

In this determination lard A and beef suet again show the same sign in change. The change in Sample No. 6 is markedly negative, while the others are positive. The increase in 7, 8, 9 and 10 seem to bear no noticeable relation to the time.



## Reichert-Meissel Determinations.

Samp. No.	Wt. of Fat taken grs.	NaOH Used for 100cc. cc.	R-W Val. cc. n/10 NaOH per 5grs. Fat	Average
4A	9.7474	1.95	1.77	
4B	2.6931	.55	1.81	1.79
6A	5.4474	1.25	2.01	
6B	4.5914	1.05	2.03	2.02
8A	4.9279	.95	1.71	
8B	4.8855	.90	1.64	1.68
7A	5.2100	.70	1.19	
7B	5.1302	.65	1.12	1.16
9A	3.9501	.87	1.95	
9B	5.6053	1.23	1.95	1.95
11A	5.0905	1.03	1.80	
11B	4.4719	.86	1.71	1.76
10A	4.7549	.75	1.39	
10B	5.5324	.90	1.44	1.42
12B	4.6836	.58	1.10	
12A	6.8802	.83	1.07	1.09

1 cc. standard NaOH = 1.775 cc. n/10 NaOH.



Rearranged, this table shows the following.

Samp. No.	Hours Heated	Reichert- Meissel Value	Difference
4	0	1.79	
6	7 1/2	2.02	+ .23
7	0	1.16	
8	7	1.68	+ .52
9	10 1/3	1.95	+ .79
10	16 1/3	1.42	+ .26
11	0	1.76	
12	3 1/4	1.09	- .67

This is the first instance in which the two samples of lard have given regular variation of the same sign. The increase in 8 and 9 seems to be proportional to the time, while the lower result for 10 may be due to changes into soluble nonvolatile acids, and will account for the marked increase in that determination.





## SUMMARY

Samp. No.	Time Heat.	Spec. Grav.	Tot. Free Acid Val.	Acids Oleic Acid	I Ab-sorb. No.	Free Vol. Acids	Sol-uble Acids	Insol. Acids	Reich-ert - Meis-sel Value
4	0	.8939	.444	.32	48.46	.442	.239	93.14	1.79
6	7 1/2	.8981	3.965	2.855	52.19	.369	.459	79.53	2.02
Dif.		<u>+.0042</u>	<u>+3.521</u>	<u>+2.535</u>	<u>+3.73</u>	<u>-.073</u>	<u>+.220</u>	<u>-13.61</u>	<u>+.23</u>
7	0	.8946	.444	.32	55.78	.396	.492	95.24	1.16
8	7	.8993	5.28	3.76	51.85	.601	.119	95.52	1.68
Dif.		<u>+.0047</u>	<u>+4.836</u>	<u>+3.44</u>	<u>-3.93</u>	<u>+.205</u>	<u>-.373</u>	<u>+.28</u>	<u>+.25</u>
9	10 1/3	.8937	1.44	1.015	41.53	.376	.467	96.28	1.95
Dif.		<u>-.0009</u>	<u>+1.00</u>	<u>+.695</u>	<u>-14.25</u>	<u>-.020</u>	<u>-.025</u>	<u>+ 1.04</u>	<u>+.79</u>
10	16 1/3	.8954	2.645	1.88	36.41	.436	1.724	95.74	1.42
Dif.		<u>+.0008</u>	<u>+2.201</u>	<u>+1.56</u>	<u>-19.37</u>	<u>+.040</u>	<u>+1.232</u>	<u>+.50</u>	<u>+.26</u>
11	0	.8915	.700	.495	32.56	.439	.321	94.66	1.76
12	3 1/4	.8945	4.91	3.495	30.94	.365	.308	96.24	1.09
Dif.		<u>+.0030</u>	<u>+4.21</u>	<u>+3.000</u>	<u>-1.62</u>	<u>-.074</u>	<u>-.013</u>	<u>+ 1.58</u>	<u>-.67</u>



## SUMMARY

The difference in behavior of the three fats under the influence of heat seems to indicate that the nature of the decomposition is dependent upon the kind and character of the fat.

For lard B the temperatures range from 180°-275° under ordinary conditions. For lard A it is 265°-304°.

A sudden rise in temperature from 304°-20° above 360° is noted in the case of lard A. As yet this is unexplainable.

Some of the temperatures registered in the experiments seem to indicate the formation and distillation of n-valeric acid, n-caproic acid, oenanthylic acid and caprylic acid.

The results of the analyses seem to confirm the opinion that the nature of decomposition is dependent upon the kind and character of the fat.

The specific gravity increases largely in all cases but one.

Total free acids also show a very large increase in every case.

The iodine absorption number increases in the case of lard B and decreases in that of lard A and beef suet. Lard A shows a markedly regular decrease with increase of time.

Two of the fats show a decrease in free volatile acids, while the third, but for one sample, shows an increase.

Lard B increased in soluble acids, while lard A in two cases showed a decrease and in the third a marked increase. Beef suet likewise shows a decrease.

Insoluble acids increased in all cases but that of lard B, where the decrease is large.

The Reichert-Meissel value increased in all but the beef suet.



Sample No . 9 is irregular in all the determinations, seeming to indicate that there is a radical chemical change after 10 hours heating. Equilibrium seems to have been partially reestablished after 16 hours. The iodine number seems not to have been disturbed, but the free volatile and soluble acids exhibit a marked increase. The insoluble acids and Reichert-Meissel value, however, partially regain their positions.

These results only partially confirm the work of Spaethe who records<sup>8</sup> an increase in volatile acid and a decrease in iodine number upon the oxidation of fats.

### CONCLUSIONS

The experimental data herewith presented seem to indicate that:

1. When fats are decomposed by heat there are certain well defined temperatures at which the decomposition takes place. These temperatures seem to be dependent on the kind and character of the fat and the initial freshness.

2. There is a change in the chemical constants occasioned by the heating of fats to high temperatures. This change also seems to be dependent upon the kind and character of the fat, and to bear some relation to the length of the period of heating.

3. This method gives promise of an insight into the chemical changes which take place when fats are decomposed by heat.





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